

Supporting Information

A Robust Damage-Reporting Strategy for Polymeric Materials Enabled by Aggregation-Induced Emission

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Materials and general methods

Polyurethane prepolymer (PU, Desmodur L 75) was obtained from Bayer MaterialScience. Ethylene maleic anhydride copolymer (EMA, Zamac-400, average molecular weight of 400,000 g/mol) was obtained from Vertellus (Indianapolis, IN). EPON epoxy resin 813 (74% diglycidyl ether of bisphenol-A and 26% o-cresyl glycidyl ether) and curing agent EPIKURE 3233 (polyoxypropylene triamine) were obtained from Miller-Stephenson (Houston, TX). Polyurethane coatings were prepared using a two-part acrylic polyurethane (Interthane 990, International Paint). Polydimethylsiloxane (PDMS) coatings were prepared using a two-part Sylgard 184 Silicone Elastomer (Dow Corning). Irgacure 250 photoinitiator (BASF) was used for the cationic polymerization of EPON resin 813 to prepare UV-cured epoxy coatings. Polystyrene (average molecular weight of 280,000 g/mol), polyacrylic acid (35 wt% in water, average molecular weight of 100,000 g/mol), and all of other chemicals were obtained from Sigma-Aldrich and used as received. Carbon fiber reinforced composites (404-11-Plate-Twill, 0.115 inches thick) were obtained from Rock West Composites and cut into 2 inch squares using a diamond saw.

UV-vis absorption spectra were measured from solutions of TPE in hexyl acetate (Shimadzu UV-2401PC spectrometer) with concentrations ranging from 66 μM to 26 mM. Fluorescence spectra of TPE were recorded from the solid deposited on a glass slide after evaporation of an ethyl acetate solution (Horiba FluoroMax-4). Thermal behavior of microcapsules was characterized by thermogravimetric analysis (TA Instrument Q50) with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen.

Preparation of microcapsules

Polyurethane/poly(urea-formaldehyde) double-shell-wall microcapsules containing a hexyl acetate solution of TPE were prepared using a single batch process.¹ Briefly, 0.83 g of urea, 83 mg of ammonium chloride, 83 mg of resorcinol, and two drops of 1-octanol were combined with 42 mL of a 0.5 wt% EMA aqueous solution. Under continuous mechanical agitation at 800 rpm, the core solution consisting of 174 mg TPE, 20 mL hexyl acetate, and 670 mg PU was slowly added to the aqueous mixture and allowed to emulsify for 10 min. Afterward, 2.1 g of formaldehyde (37% in water) was introduced and the reaction temperature was increased at a rate of 1 °C/min to 55 °C, and then maintained for 4 h. The prepared microcapsules were filtered, gently rinsed with deionized water to remove excess surfactant, dried, and sieved to isolate a certain size range. Microcapsules with a diameter of $112 \pm 10 \mu\text{m}$ were used for damage indication studies. Control microcapsules (diameter of $112 \pm 13 \mu\text{m}$) were prepared using an identical procedure, emitting TPE from the core solution. Note that heating was required to dissolve TPE in hexyl acetate and produce optically clear solutions. Under ambient conditions, bulk solutions with TPE concentrations $\geq 0.9 \text{ wt\%}$ (24 mM) exhibited some precipitation after prolonged time; however, no evidence of aggregation or precipitation was observed for encapsulated solutions (1 wt% TPE) or bulk solutions with concentrations $\leq 0.82 \text{ wt\%}$ (21 mM) over a period of several months.

Fabrication of coatings

Epoxy coatings were prepared by mixing a stoichiometric ratio of EPON 813 epoxy resin and EPIKURE 3233 curing agent (weight ratio of 100:43) with microcapsules added into the mixture at various weight percentages. The well-mixed dispersions were coated on glass slides or carbon

fiber reinforced polymer composite substrates using a micrometer controlled doctor blade and cured at 35 °C for 24 h. Polyurethane and polydimethylsiloxane coatings were prepared in a similar fashion. UV-cured epoxy coatings were prepared using 5 wt% photoinitiator (Irgacure 250) and cured for 4 h under a 365 nm UV lamp (25 W Cole-Parmer UV Transilluminator). Polystyrene coatings were prepared by mixing a 30 wt% solution of polystyrene in toluene with 10 wt% microcapsules (with respect to polystyrene) and drop casting the well-mixed dispersion onto glass slides. The coatings were allowed to dry at room temperature for approximately 24 h inside a loosely covered glass dish to control the rate of solvent evaporation. Polyacrylic acid coatings were prepared similarly using a 35 wt% aqueous solution of polyacrylic acid.

Characterization of coatings

Coatings were examined using fluorescence light microscopy (Zeiss Observer Z1 inverted microscope with 350EX/460EM DAPI Chroma filter set 31000V2), stereomicroscopy (Zeiss SteREO Discovery V20 microscope), and scanning electron microscopy (Philips XL30 ESEM-FEG). Photographic images were acquired using a Canon EOS 7D digital camera equipped with a 425 nm longpass filter under ambient room lighting and illumination with a handheld UV source (OPTI-LUX 365 Series, Spectronics Corporation). Reproducible scratches were created in epoxy coatings using a test panel scratcher (Corrocutter 639, Erichsen) with the scratch depth controlled by adjusting the load applied on the stylus. Scratch depths were measured using cross-sectional images obtained from microCT in five locations along the length of each scratch to provide an average depth and standard deviation as follows: $94 \pm 24 \mu\text{m}$; $140 \pm 16 \mu\text{m}$; $171 \pm 12 \mu\text{m}$; $222 \pm 38 \mu\text{m}$; $376 \pm 30 \mu\text{m}$.

Image analysis

Fluorescence micrographs were processed with Fiji.² Plots of fluorescence intensity were generated in Origin Pro 2015 after applying a 3D smoothing function. Integrated intensities were measured by extracting individual scratches with equal area, dividing the images into at least 20 equal segments, and measuring the integrated density of each segment to provide an average and standard deviation. For the time-dependent fluorescence measurements, images were recorded at approximately 20 s intervals after scratching the coating with a razor blade. Images were cropped to the same pixel dimensions, background subtracted, and the integrated intensity was measured for the entire image containing the scratched region of the coating.

X-ray computed microtomography

MicroCT images were acquired on an Xradia BioCT (MicroXCT-400). 360 degree scans were obtained in rotation intervals of 0.4° using a 4x objective at 7 s exposure times with 40 keV (8 W, 200 μ A). 3D image reconstructions were performed using TXM Reconstructor (v.8.1, Xradia) and visualized in 3D with TXM3Dviewer (v.1.1.6, Xradia). MicroCT images were post-processed in Amira (v.5.6.0, FEI).

Profilometry

Profilometry data was acquired on a KLA Tencor P-6 stylus profilometer with a 2 μ m radius tip. The scan area was 10.5 mm x 4 mm. The scanning, or x dimension was transverse to the scratch. Line scans were performed at a y spacing of 50 μ m. The scan speed was 200 μ m s⁻¹ and the sampling rate was 500 Hz. Profilometry data was processed in Matlab (Mathworks).

Impact testing

Impact damage was created on coated carbon fiber reinforced composite panels using a drop-weight tower (Dynatup 8210) equipped with a 25 mm diameter hemispherical shaped tup (striker). The drop height was 249 mm with corresponding impact energy of 10 J. The specimen was clamped into a square support fixture with a 38 mm diameter opening at the center of the panel.

References

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- (2) Schindelin, J.; Arganda-Carreras, I.; Frise, E.; Kaynig, V.; Longair, M.; Pietzsch, T.; Preibisch, S.; Rueden, C.; Saalfeld, S.; Schmid, B.; Tinevez, J.-Y.; White, D. J.; Hartenstein, V.; Eliceiri, K.; Tomancak, P.; Cardona, A. Fiji: An Open-Source Platform for Biological-Image Analysis. *Nat. Meth.* **2012**, *9*, 676–682.

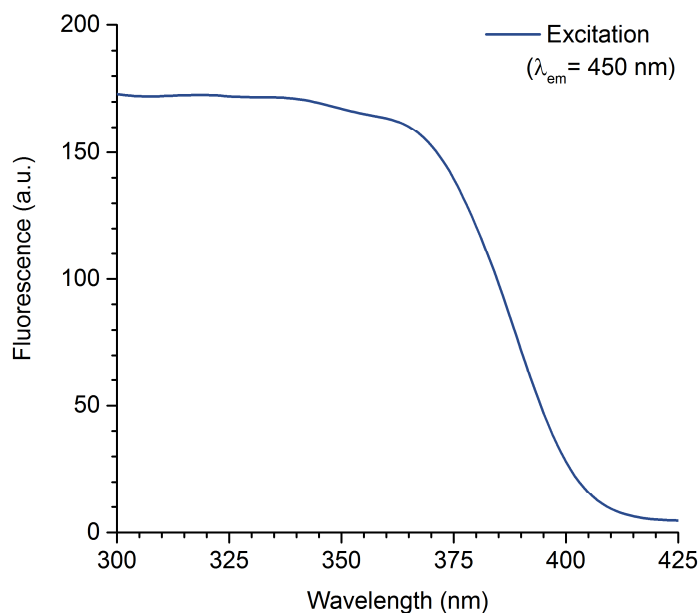


Figure S1. Fluorescence excitation spectrum of solid TPE deposited from solution by evaporation on a glass substrate. Fluorescence emission was monitored at 450 nm.

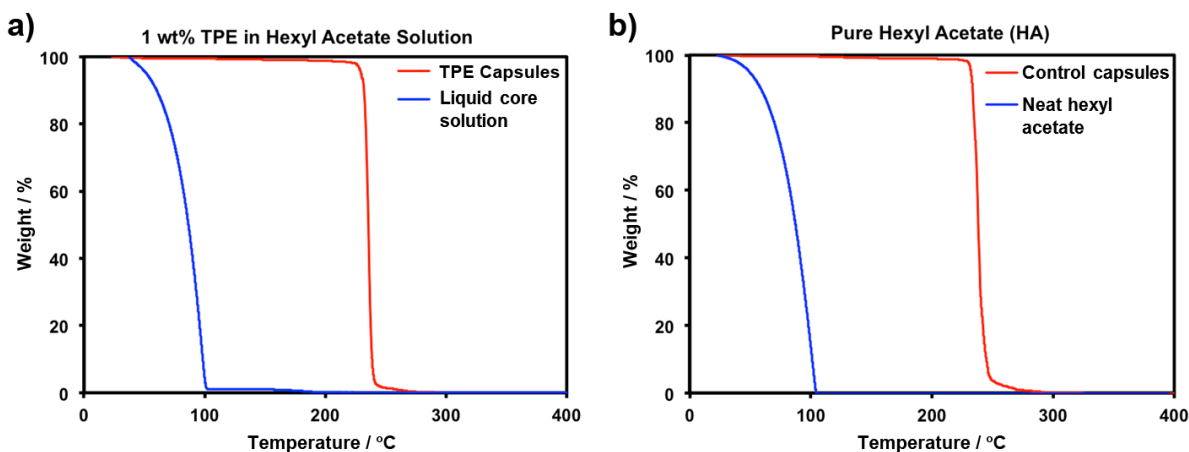


Figure S2. Thermogravimetric analysis of (a) TPE microcapsules containing 1 wt% TPE in hexyl acetate in the core, and (b) control microcapsules containing only hexyl acetate demonstrates significantly enhanced thermal stability up to 220 °C compared to the unencapsulated core solutions (blue traces).

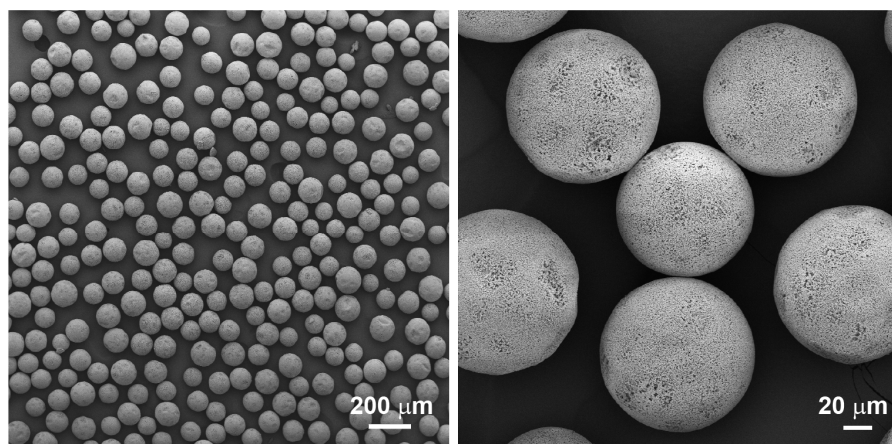


Figure S3. SEM images of TPE microcapsules with diameter of $112 \pm 10 \mu\text{m}$.

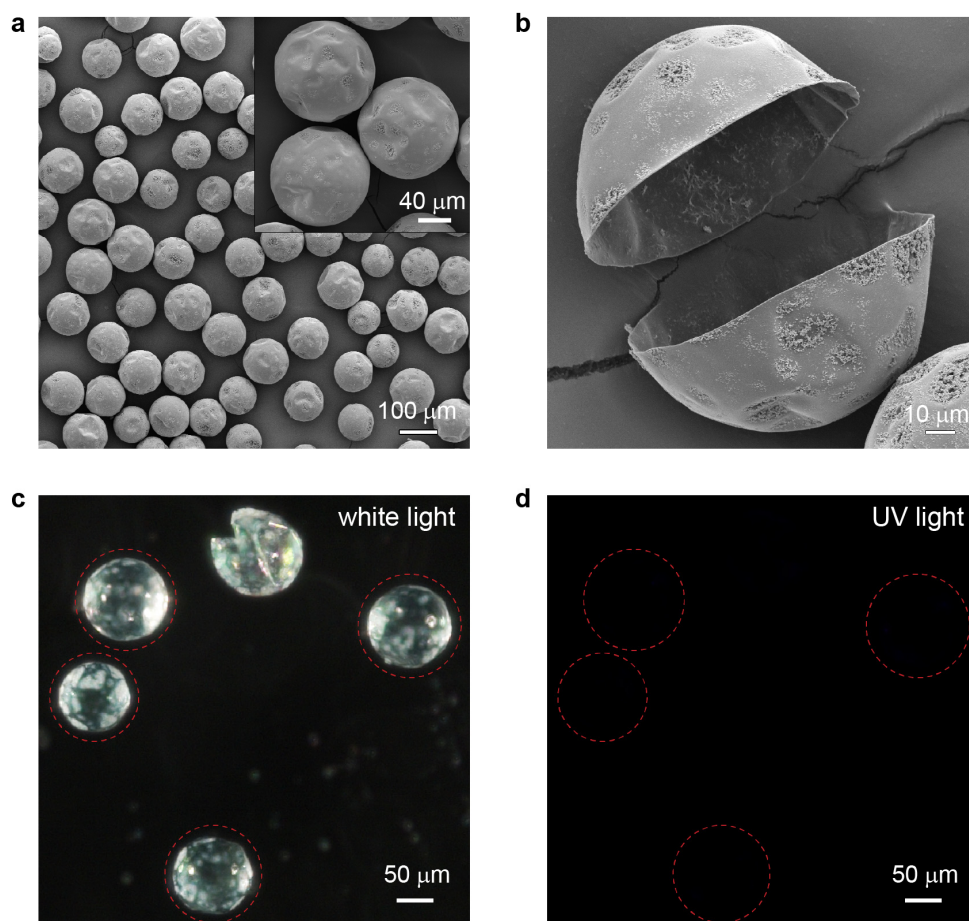


Figure S4. SEM images of (a) intact and (b) ruptured control microcapsules containing only hexyl acetate in the core (diameter of $112 \pm 13 \mu\text{m}$). Micrographs of control microcapsules under (c) white light and (d) UV light. Under UV light, both the intact (red dashed circles) and ruptured microcapsules are undetectable.

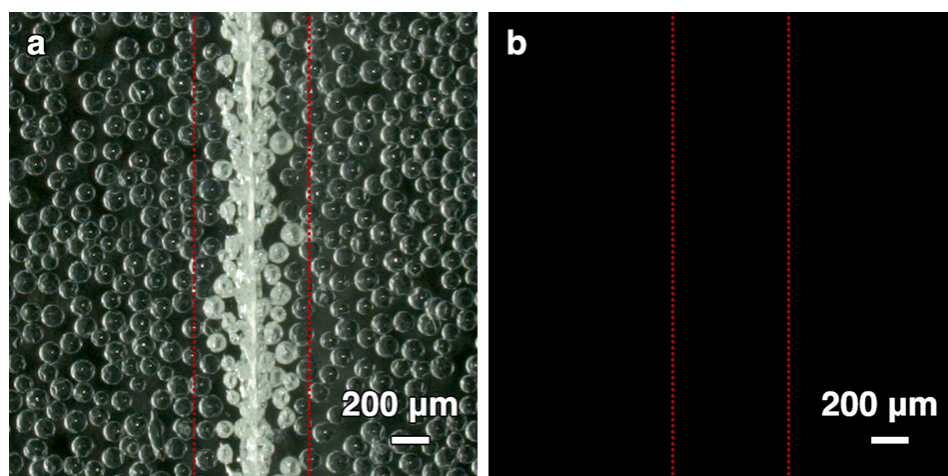


Figure S5. Micrographs of epoxy coating incorporating 10 wt% control microcapsules after being scratched with a razor blade under (a) white light and (b) UV light. No fluorescence was observed under UV light from the damaged coating. As a visual guide, the location of damage is indicated by the area inside of the dashed red lines.

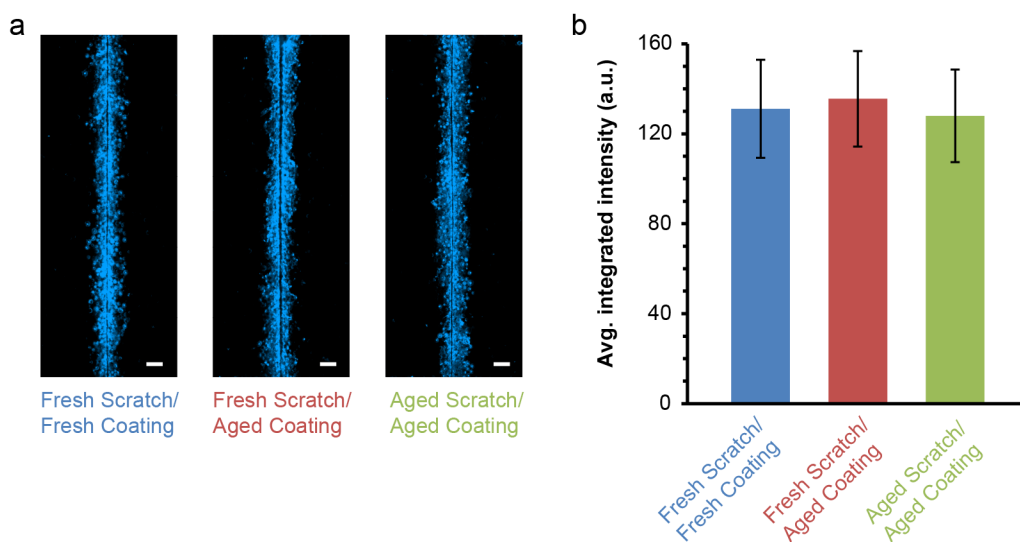


Figure S6. Stability of damage indication performance. (a) Fluorescence micrographs of epoxy coatings containing 10 wt% TPE microcapsules at various time increments (scale bars, 250 μm). (b) The fluorescence response was quantified for a freshly prepared and scratched coating, a coating prepared and damaged 44 days previously (stored in ambient conditions), and the same aged coating that was scratched immediately prior to analysis, with each demonstrating equivalent indication.

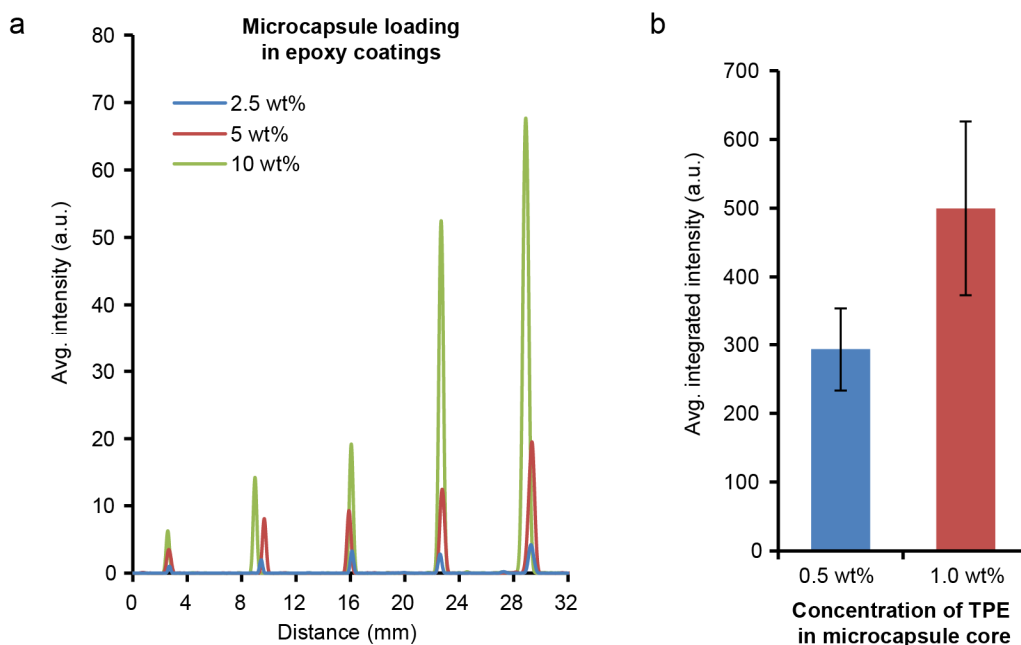


Figure S7. Effect of TPE concentration and microcapsule loading on damage indication performance in epoxy coatings. Coatings were scratched and then analyzed using fluorescence microscopy. (a) Fluorescence intensity profiles for epoxy coatings containing 2.5, 5, or 10 wt% TPE microcapsules (core concentration of 1 wt% TPE in hexyl acetate) with various scratch depths. Average scratch depth from left to right: 94, 140, 171, 222, and 376 μm . (b) Scratched epoxy coatings containing 10 wt% TPE microcapsules (diameter of $57 \pm 8 \mu\text{m}$) with core solution concentrations of 0.5 wt% (13 mM) or 1.0 wt% (26 mM) TPE in hexyl acetate.

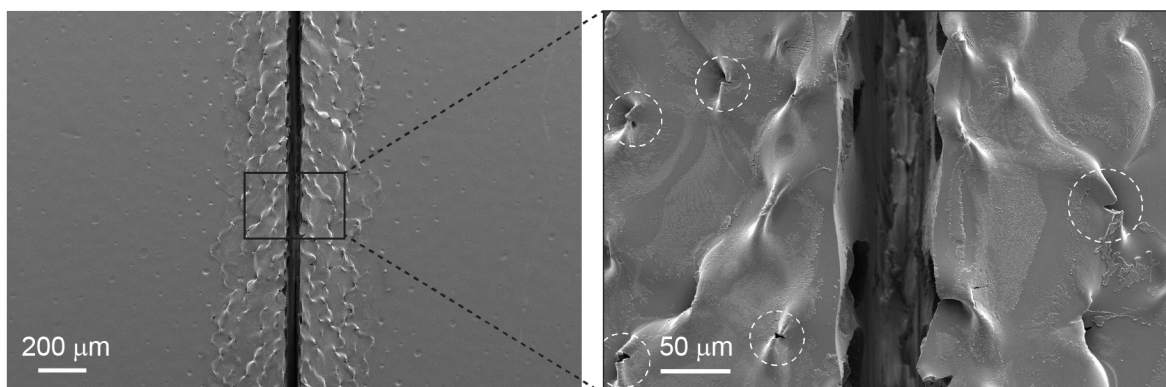


Figure S8. SEM images of epoxy coating containing 10 wt% TPE microcapsules showing ruptured microcapsules at the surface of the sheared region adjacent to the primary scratch damage (marked with white dashed circles).

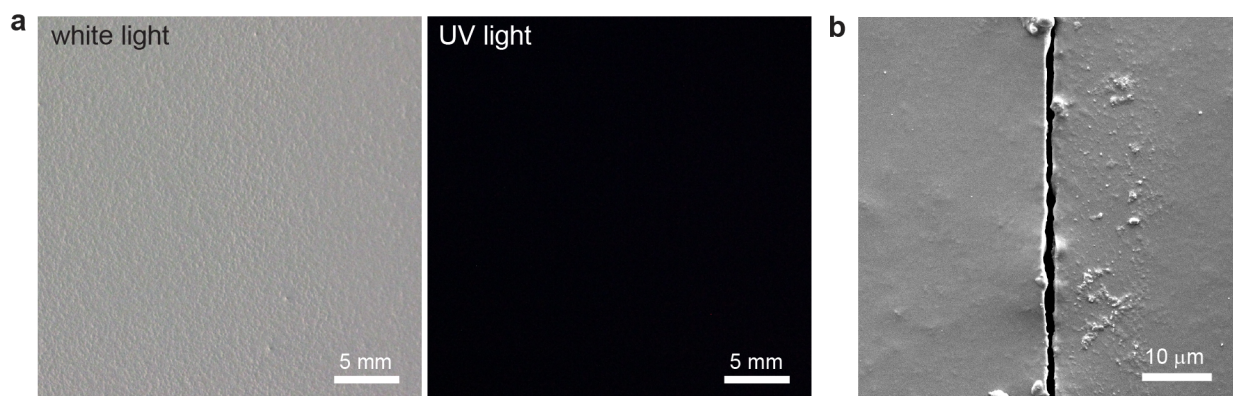


Figure S9. (a) Photographs under illumination with white light and UV light of a polyurethane coating containing 10 wt% control microcapsules after being scratched with a razor blade; (b) SEM image of the same polyurethane coating showing the scratch damage. The scratch damage is undetectable without equipment-aided visualization.

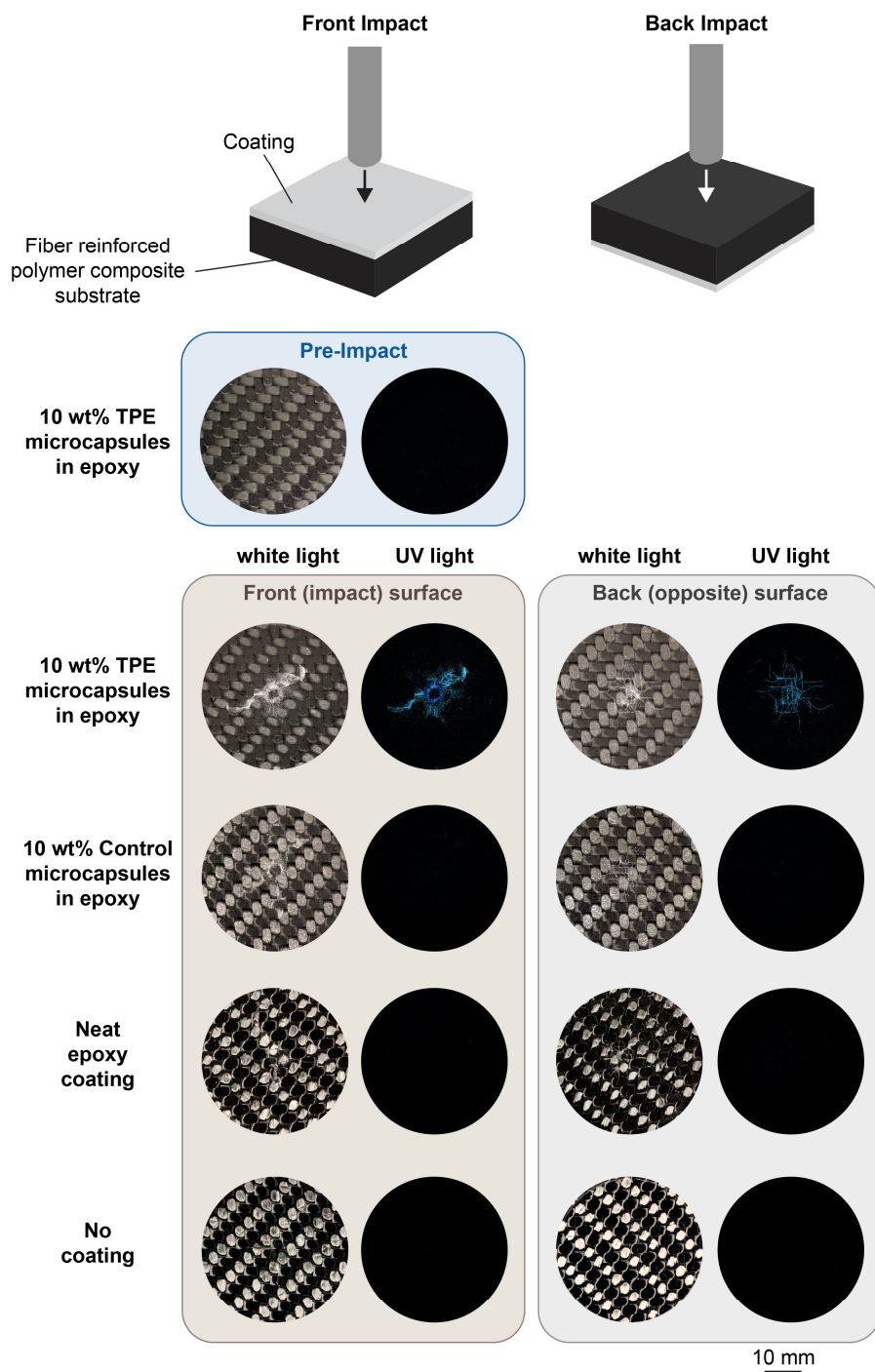


Figure S10. Photographs of carbon fiber reinforced composites with various coatings after impact damage under white light and UV light. The schematic above illustrates the two different impact damage procedures.